



# NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: ACTIVE MATERIALS ADVANCEMENTS

## Silicon Deep Dive



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U.S. DEPARTMENT OF ENERGY  
VEHICLE TECHNOLOGIES OFFICE  
2018 ANNUAL MERIT REVIEW

**Project ID # BAT352**

# OVERVIEW

## Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 55%

## Budget

- Total project funding:
  - FY18 - \$3600K
- Presentations:  
BAT349, BAT350, BAT351,  
BAT352, and BAT353

## Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

## Partners

- Sandia National Laboratories
- Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

# RELEVANCE

- Objectives: Stabilize the SEI - Stabilize the electrode
- Overall focus on insights into and advancement of silicon-based materials, electrodes, and cells.
- Advancements verified on life and performance of full cells using standardized testing protocols.

## Program Directly Addresses Cost and Performance Barriers and Quantifies Safety

- Elemental silicon can theoretically store  $>3500$  mAh/g.
- Battery Performance and Cost (BatPaC) Model indicates a silicon based anode coupled with a high capacity cathode lithium-ion technology presents a pathway to less than  $\$125/\text{kWh}_{\text{use}}$ .
- BatPaC also used to relate pack level benefits to program goals.
- Benefits reach diminishing returns after **1000 mAh/cm<sup>3</sup>** (electrode basis) for both cost and energy density.
- Silicon with  $<75$  wt% graphite can achieve target.

# MILESTONES AND ACTIVITIES

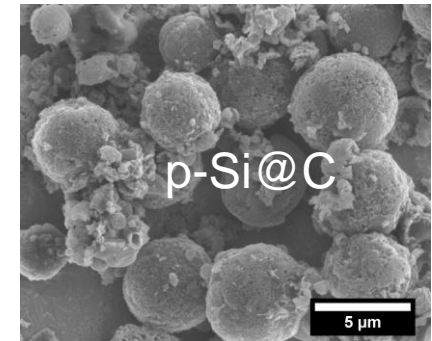
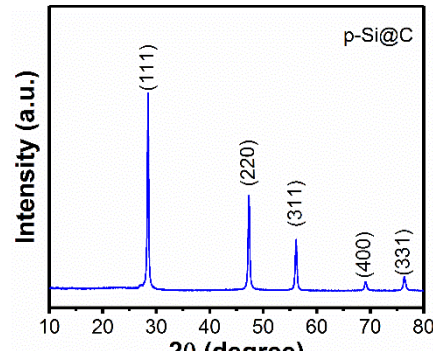
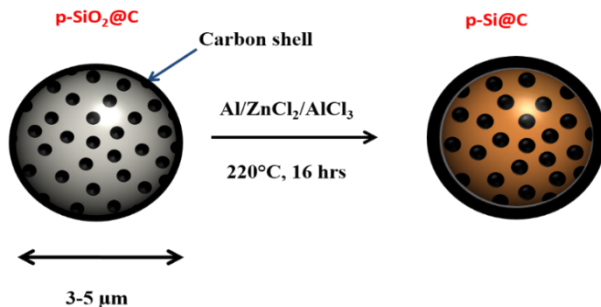
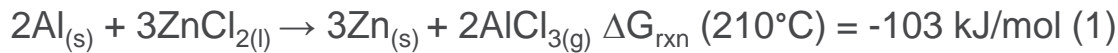
- **The program has more than twenty milestones related to the broad range of integrated activities listed below.**
- **Generally, milestones are either completed or on schedule.**
- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP); Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

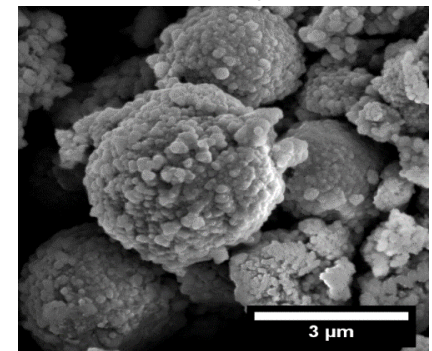
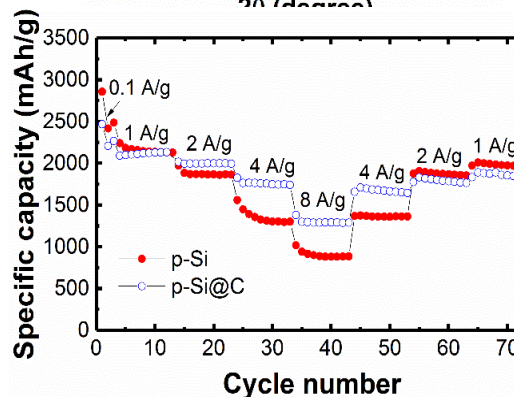
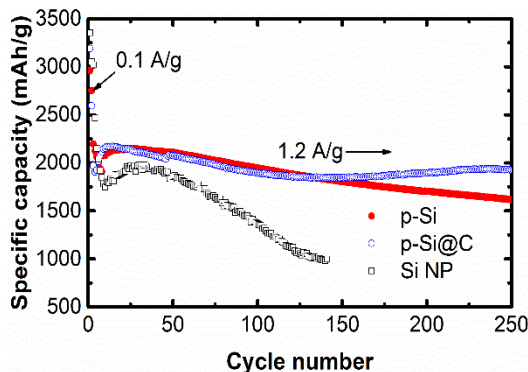
# APPROACH

- ❑ A multiple technical approach was employed to tackle the issues associated with the Si anode in this Deep-Dive program.
  - ✓ Porous Si spheres by aluminothermic reduction at  $\sim 200^{\circ}\text{C}$ .
  - ✓ Hierarchical Si/CNT microspheres as low swelling anode materials.
  - ✓ Alternative high-energy metals  $\text{Si}_{0.64}\text{Sn}_{0.36}$ .
  - ✓ Lithium silicate formation on the surface of Si particle by heat treatment.
  - ✓ Si particle surface functionalization by silane chemistry and molecular layer deposition.
  - ✓ Tailored Si/electrolyte interface by electrolytes and additives.
- ❑ Resources and scientific intelligence are shared within this consortium to promote the discovery of new materials/new technologies and facilitate the successful application of high capacity Si anode in the next generation high energy high power lithium-ion battery for electric vehicle application.
- ❑ New materials will be scaled-up with the support of MERF and incorporated into the baseline Silicon-based materials, electrodes and cells (SiBMECs) with support of CAMP and BMF. (BAT349)

# 1.1 Porous Si Spherical Particles Made by Low T (~200°C) Aluminothermite Reaction



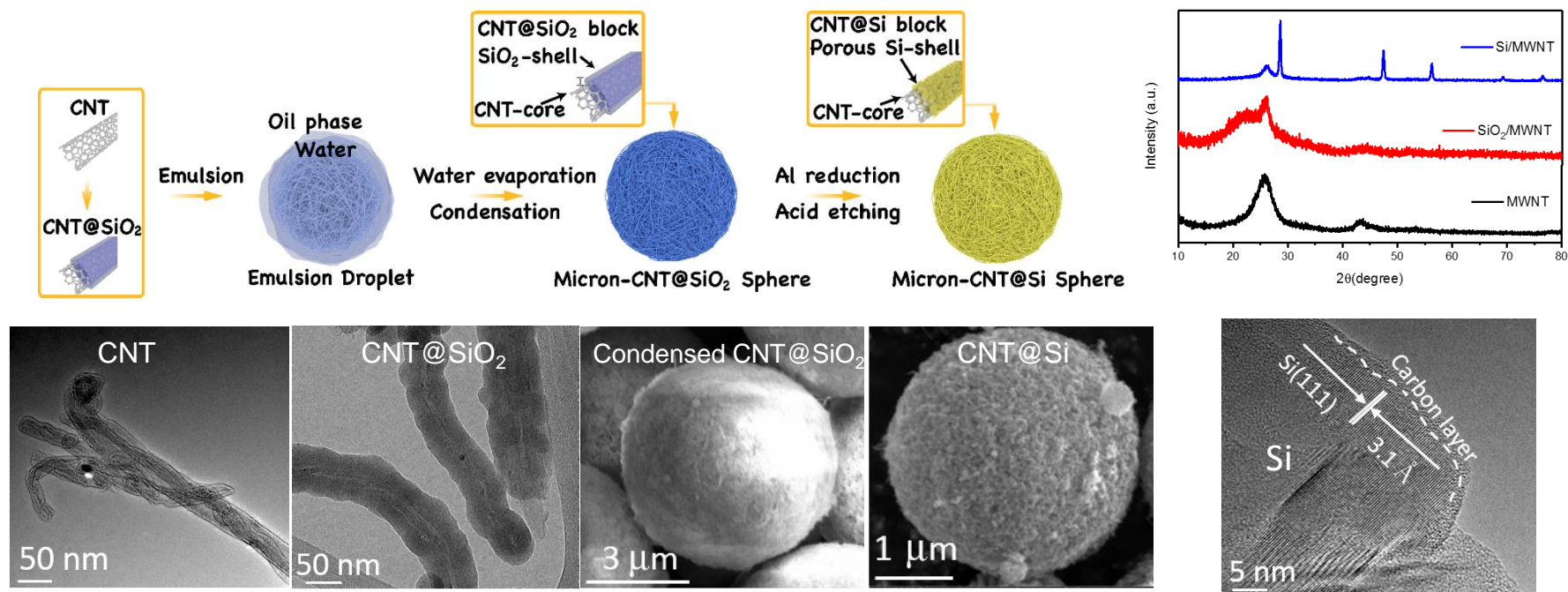
After 200 cycles



- Porous Si was obtained by aluminothermic reduction at ~200°C by using  $\text{AlCl}_3\text{-ZnCl}_2$  with a eutectic melting point of ~120°C - low cost and safe process, no formation of silicide in the magnesiothermic reduction reaction nor SiC for the reduction of  $\text{SiO}_2$ /carbon composite precursor.
- p-Si@C shows superior stability and rate capability comparing to Si NPs and retained the spherical morphology for 200 cycles.

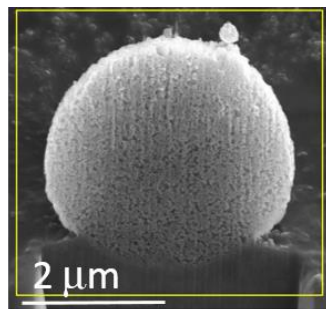
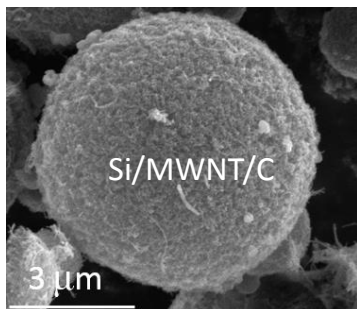
# 1.2 Hierarchical Si/CNT Microspheres

## Synthesis and characterization

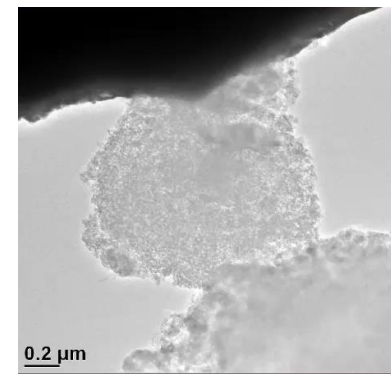
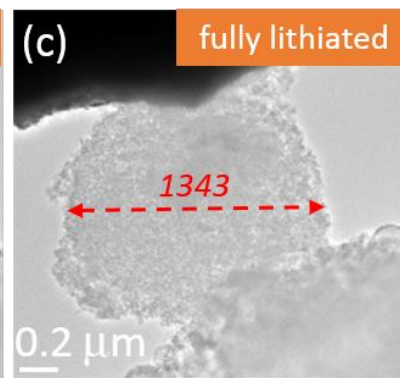
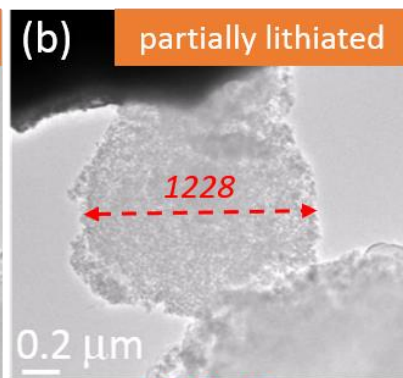
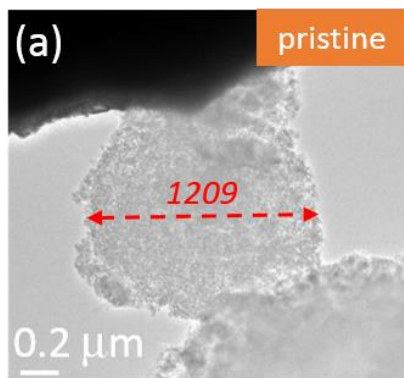


- Hierarchical Si/CNT microspheres were synthesized by aluminothermic reduction of the self-assembled SiO<sub>2</sub>-CNT microspheres.
- Micron sized Si/C composite consisting of crystalline Si coated CNT were obtained.

# Si/CNT/C Microspheres Porous Structure and Swelling Upon Lithiation



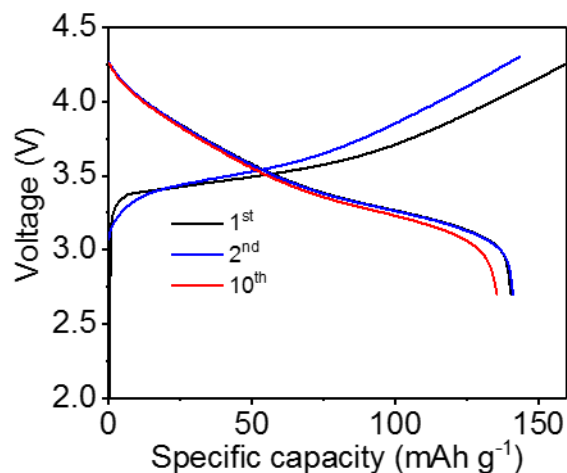
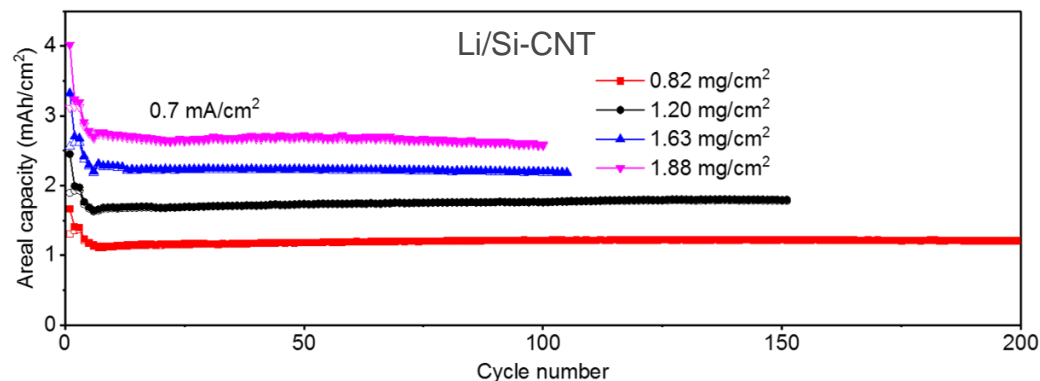
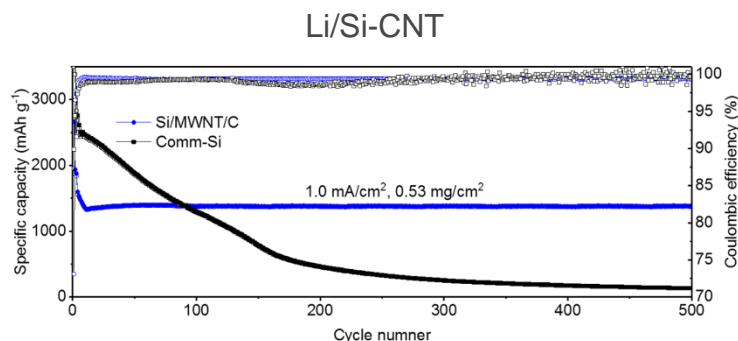
Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cc/g)	Average pore size (nm)
SiO <sub>2</sub> /MWNT	77.25	0.5	26.25
Si/MWNT	104.1	0.97	37.5
Si/MWNT/C	61.5	0.43	20.0



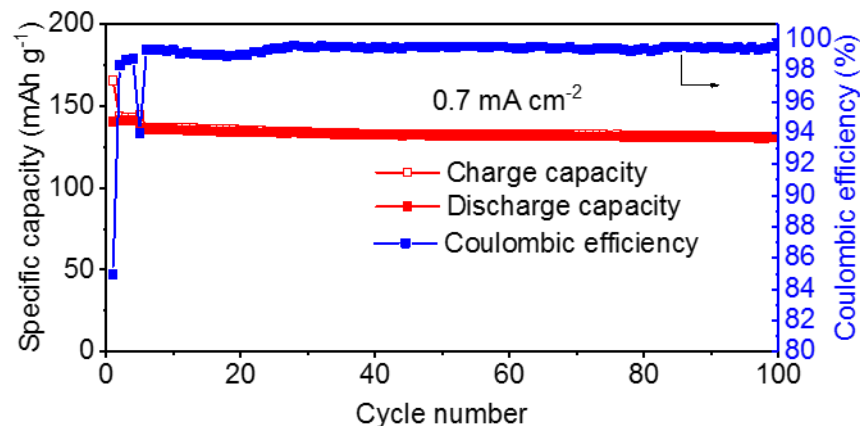
**Lithiation** →

- The Si/CNT microspheres have desired porous structure.
- *In-situ* TEM experiment shows that the Si/CNT microspheres have ~30% apparent swelling upon full lithiation.

# Electrochemical Performance: Li/Si and NMC333/Si-CNT cell



NMC333/Si-CNT



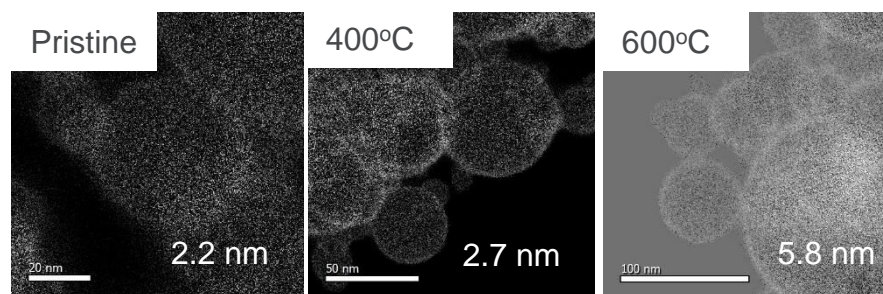
- The Si/CNT/C electrode demonstrates good cycling performance.
- The thick electrodes of  $3 \text{ mAh}\cdot\text{cm}^{-2}$  delivers  $>90\%$  capacity retention over 100 cycles.
- NMC333-preformed Si/CNT full cell shows good performance between 2.7-4.3 V.
- The capacity retention is  $\sim 90\%$  after 100 cycles

## 2. Silicate-Coated Silicon Particle (BAT348)

Silicon nanoparticles with silicate coatings with different thicknesses were synthesized. The silicate layer consists of  $\text{Li}_2\text{SiO}_3$  and  $\text{Li}_4\text{SiO}_4$

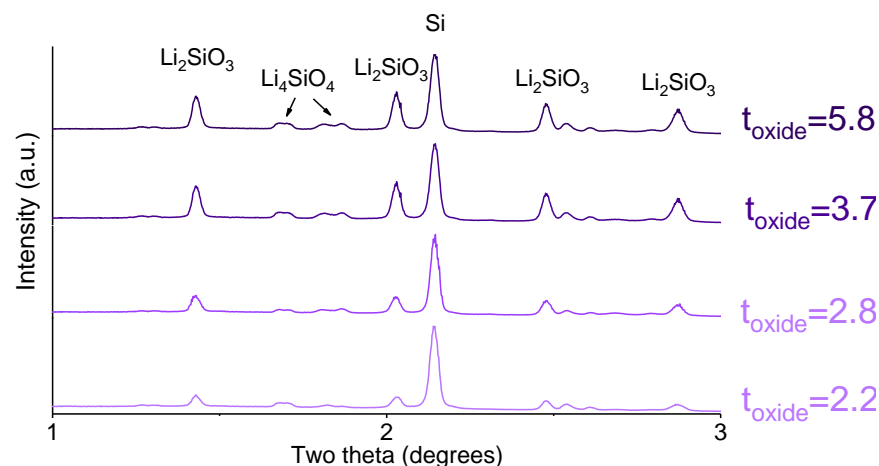


- Silicon nanoparticles with different oxide layer thickness ( $t_{\text{oxide}}$ ) were obtained via heat treatment in air



TEM oxygen K map

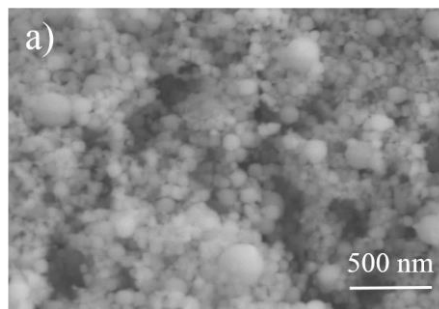
- XRD shows stronger silicate peaks with a thicker initial oxide layer



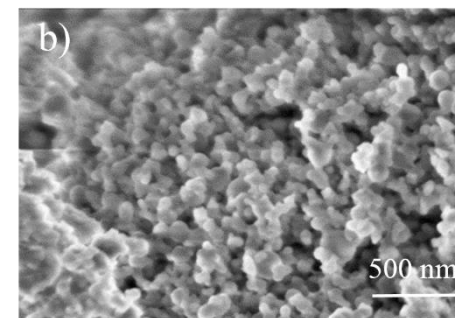
# Effect of Silicate Thickness on the Electrochemical Performance

Preliminary results showed decreased capacity with increased silicate layer thickness

Si particles before silicate reaction:



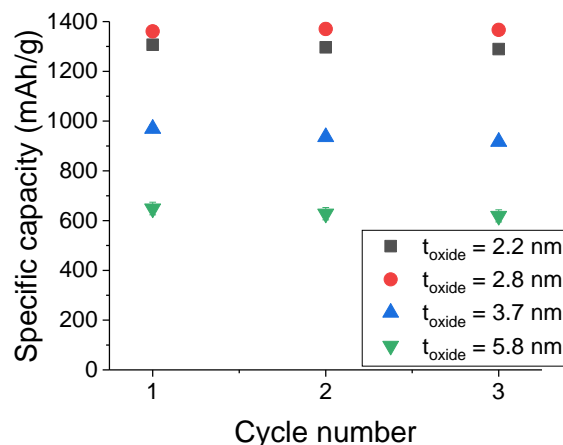
Si particles after silicate reaction:



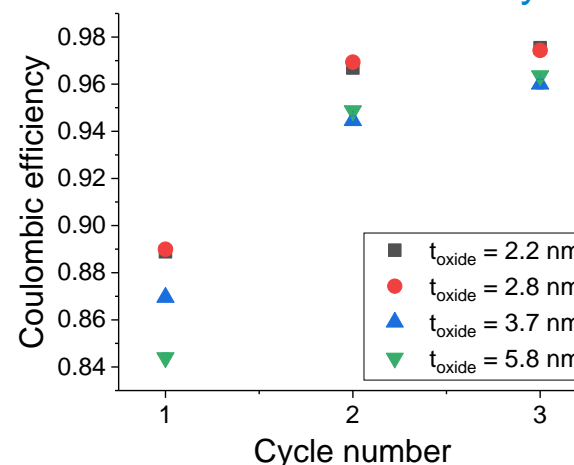
Cell testing information:

- Si: LiPAA : C45 = 70:20:10
- 0.01 – 1.5 V @ C/10, half cell
- 1.2 M LiPF<sub>6</sub> in EC:EMC=3:7, 10 wt% FEC

Specific capacity



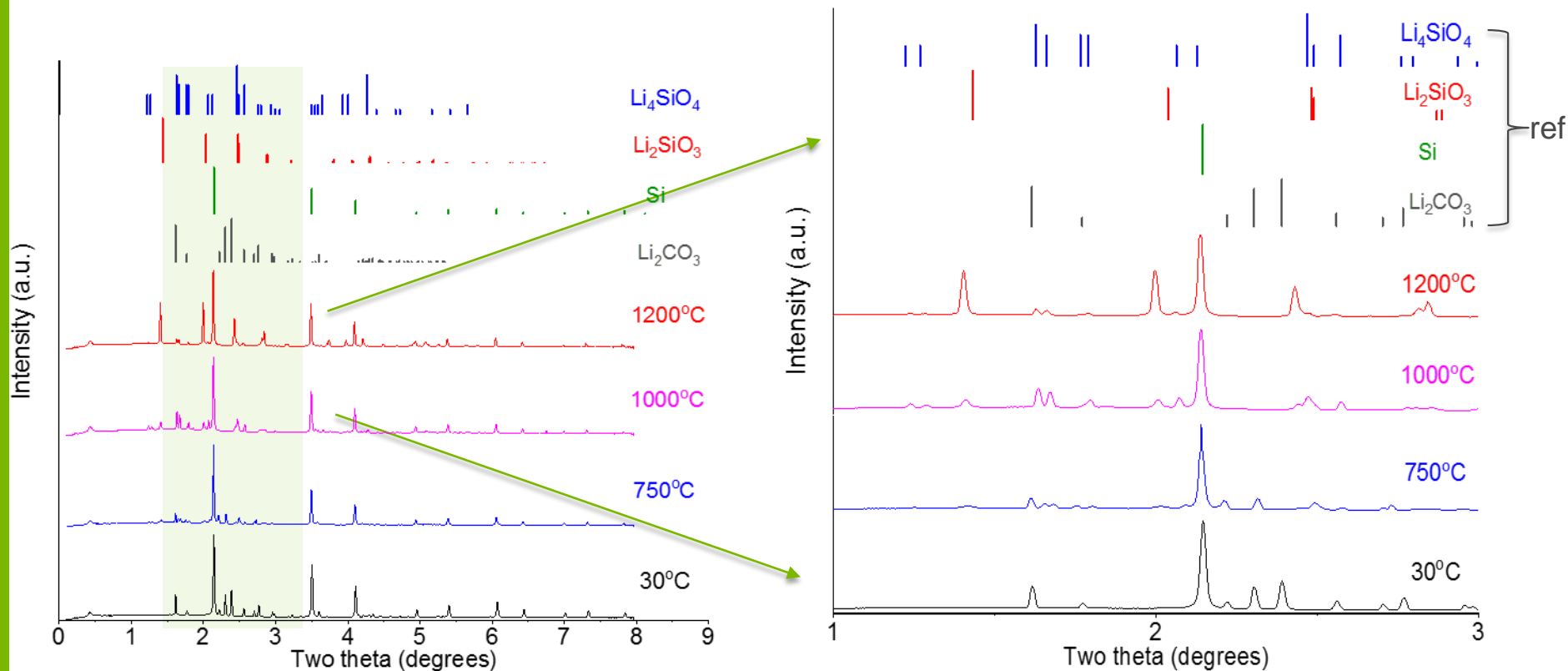
Coulombic efficiency

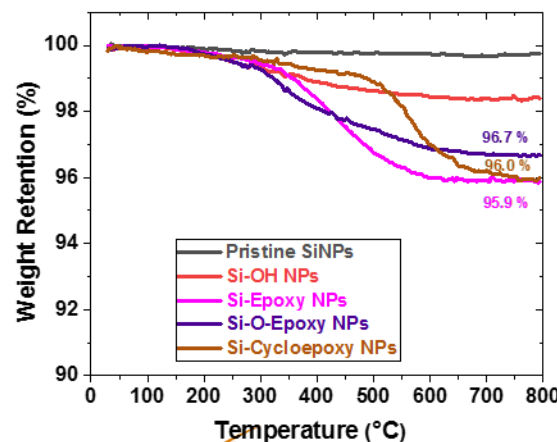
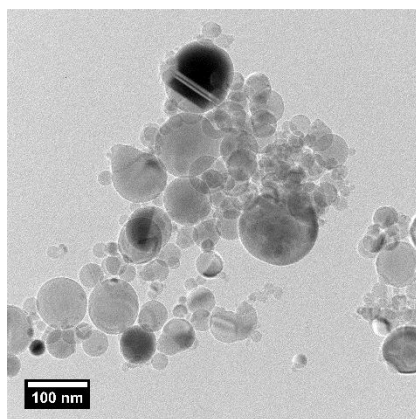
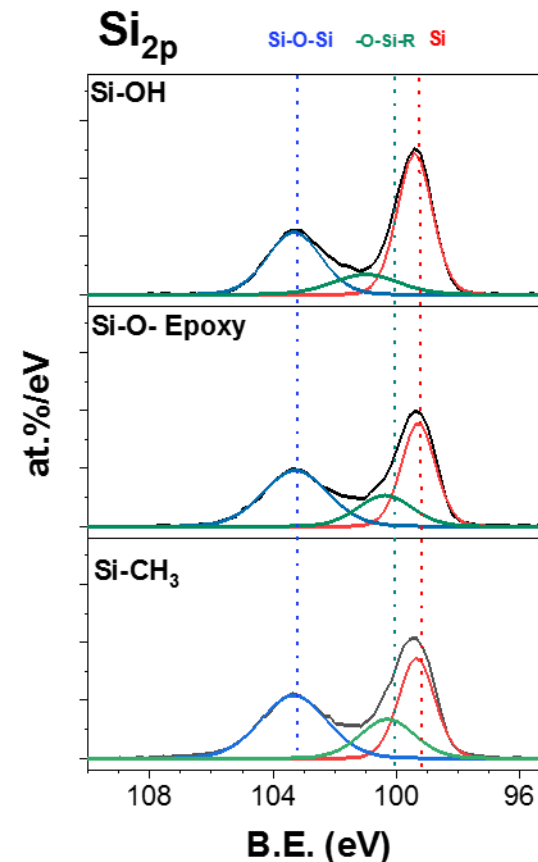
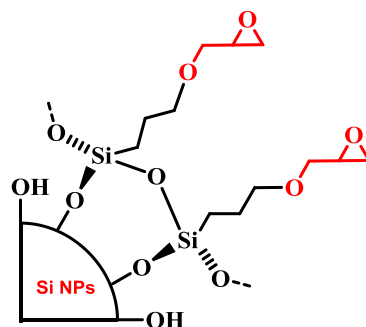
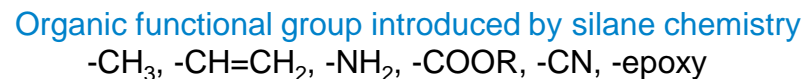


- Presence of active material aggregates is a likely cause of the compromised capacity. Further investigation is undergoing.

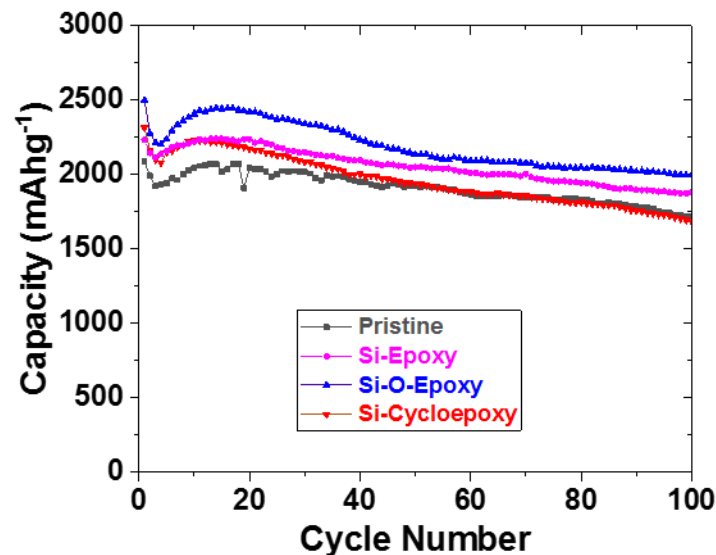
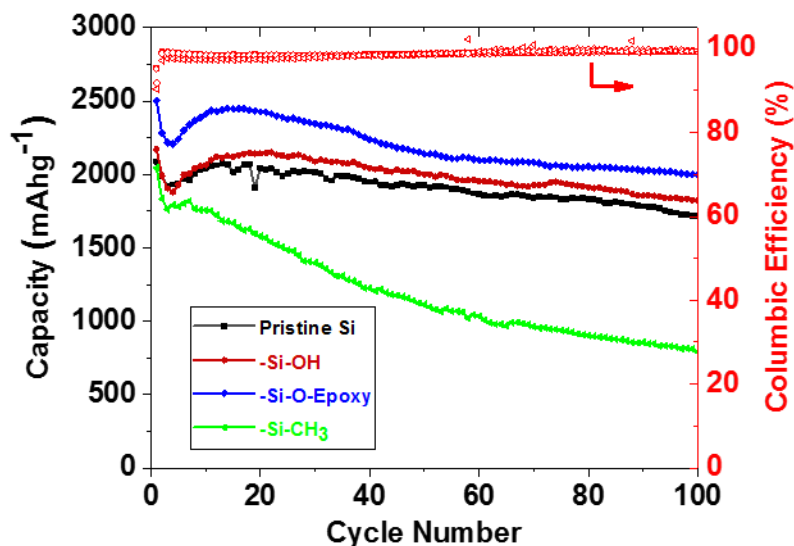
# Silicate Forming Reaction via *In-Situ* XRD

1. A mixture of  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{SiO}_3$  formed initially at lower temperature.
2.  $\text{Li}_2\text{SiO}_3$  formation then dominates, with  $\text{Li}_4\text{SiO}_4$  further converted to  $\text{Li}_2\text{SiO}_3$ .





# Impact of Functional Groups on Electrochemistry and Electrode Integrity

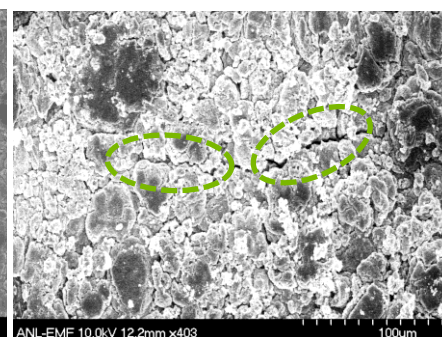
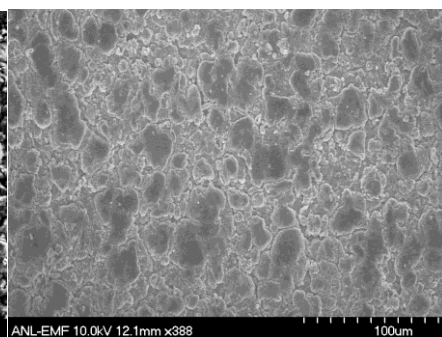
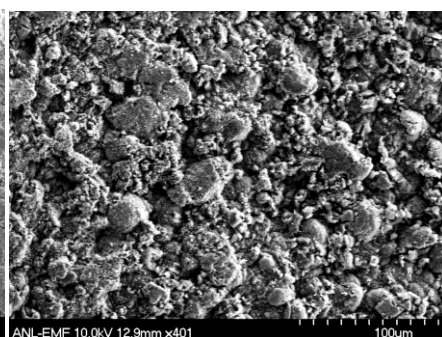
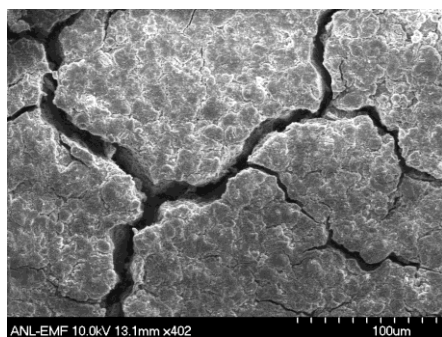


Si-Pristine

Si-OH

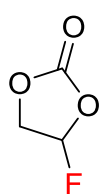
Si-O-Epoxy

Si-CH<sub>3</sub>

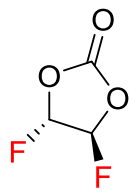


- Si electrochemical property and morphology of the cycled electrode is closely related to the functional group.
- Epoxy-functionalized Si NPs show improved cycling stability whereas the opposite effect for the Si-CH<sub>3</sub> group.
- The Si-O-epoxy NP performs the best among all studied epoxy-functionalized Si NPs.

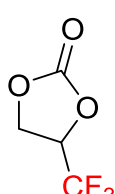
## 3.2 Tailor SEI Formation by Electrolyte and Additive



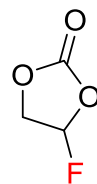
FEC



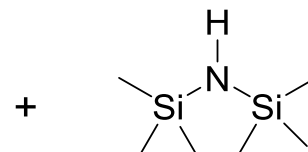
DFEC



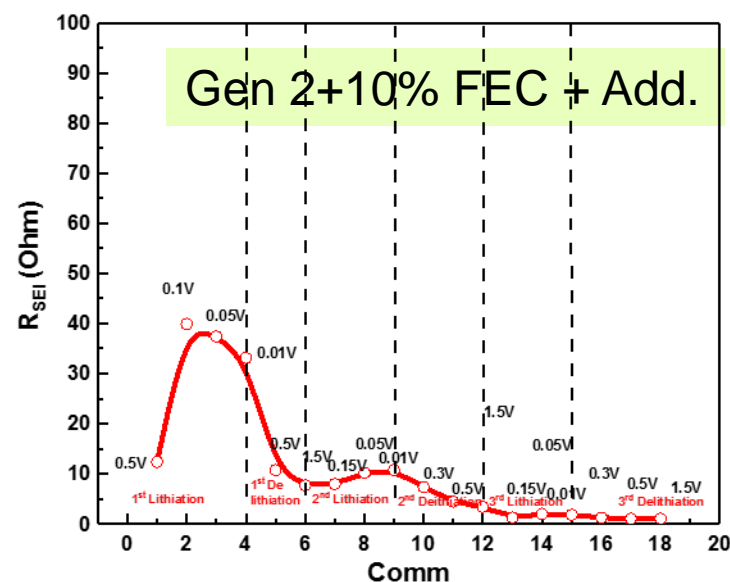
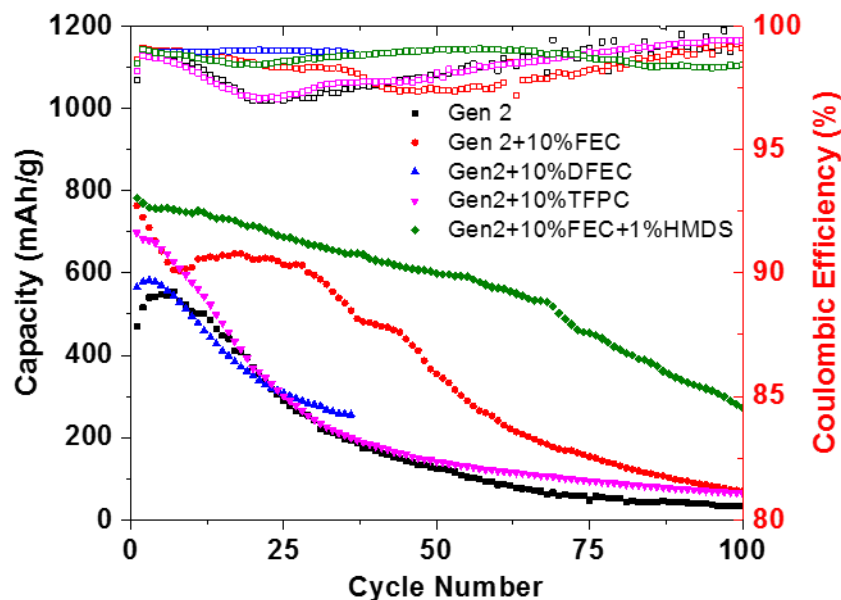
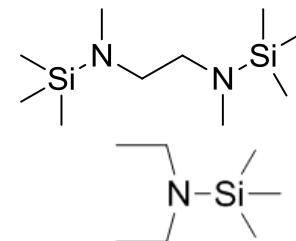
TFPC



FEC



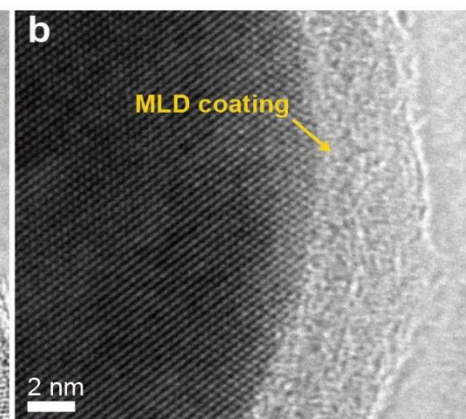
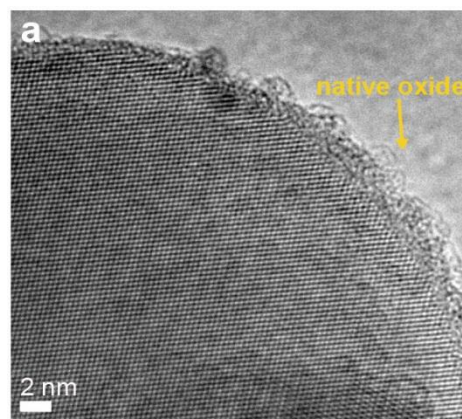
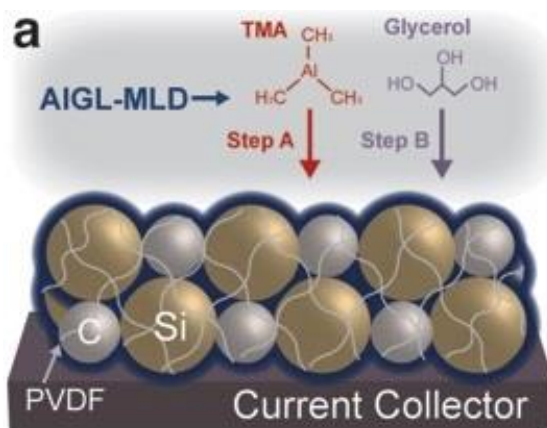
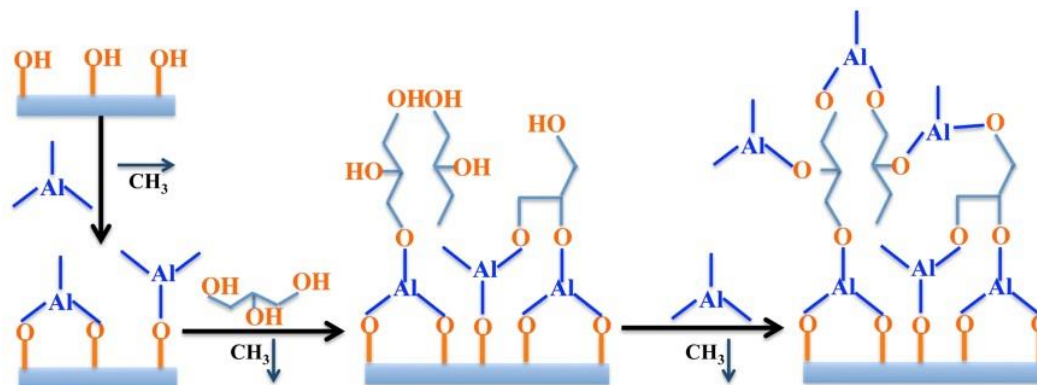
HMDS



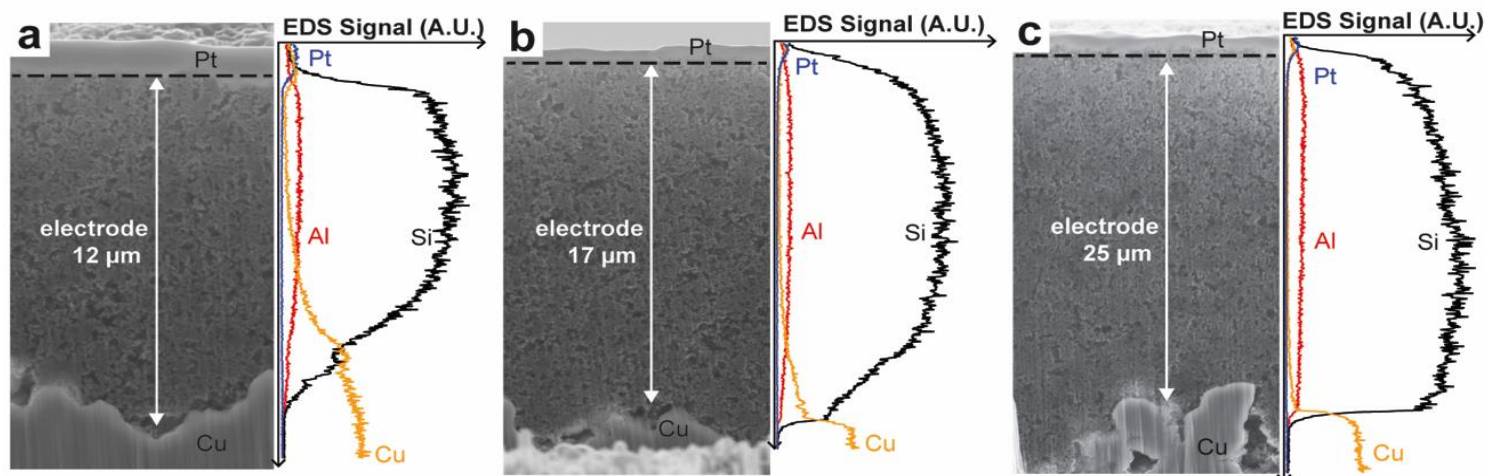
- ❑ Among fluorinated cyclic carbonates (FEC, DFEC and TFPC), FEC is the only performing additive.
- ❑ FEC/Silazane bi-additive system show the best cell performance to its synergistic effect.
- ❑ Low interfacial impedance indicates the suppression of chemical and electrochemical reaction of electrolyte.

# 4. Surface Stabilization by Molecular Layer Deposition

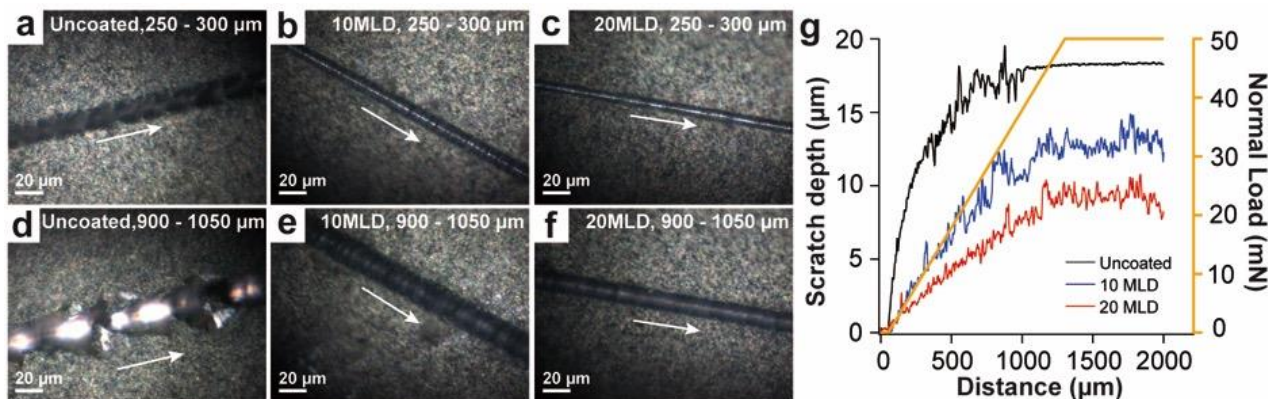
## MLD Alucone Coating: Sequential & self-limiting surface reactions enable conformal and atomic thickness control (~1 Å) (BAT347)



# MLD Coating Homogeneity and Mechanical Strength Improvement



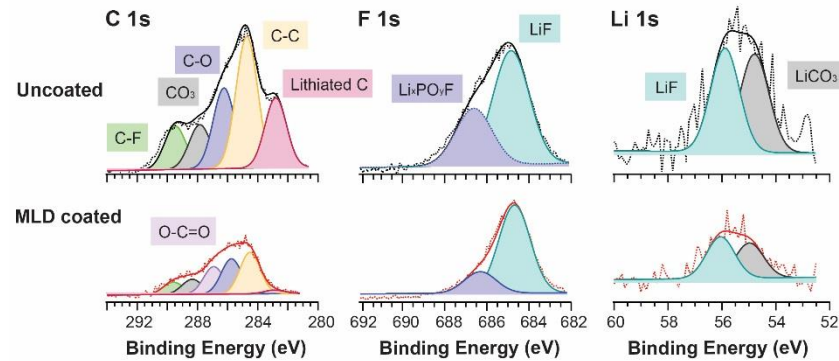
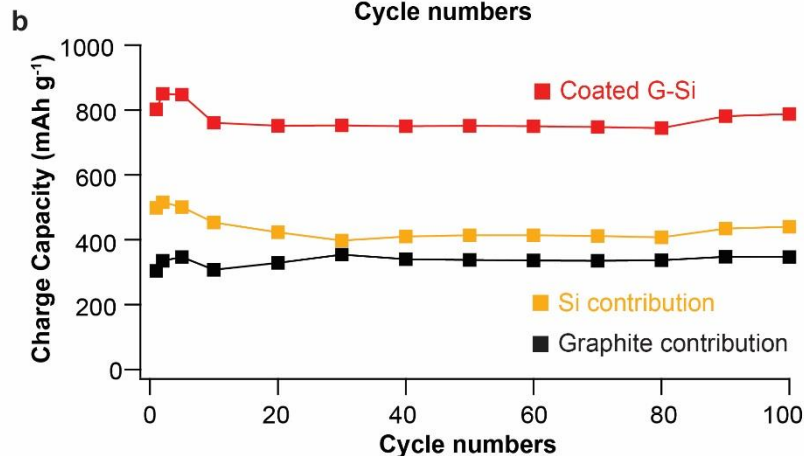
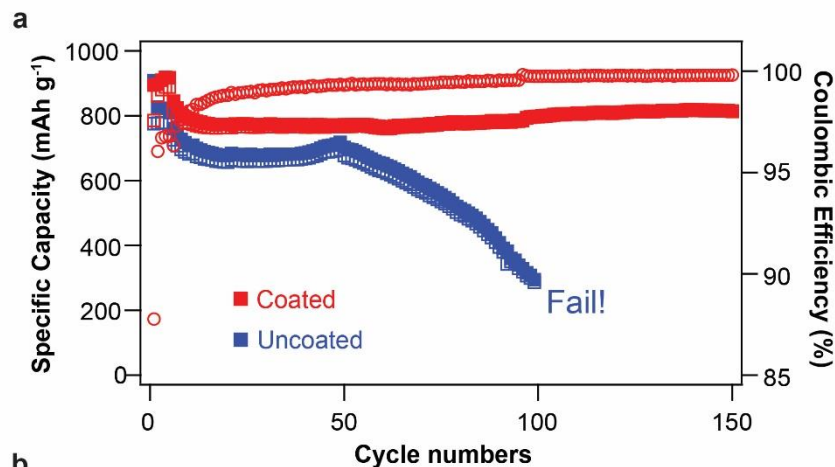
Cross-sectional SEM images of MLD coated electrodes with EDS line scanning for electrodes with different thickness and Si loading (a)  $0.43 \text{ mg/cm}^2$ , (b)  $0.63 \text{ mg/cm}^2$  and (c)  $0.79 \text{ mg/cm}^2$ .



- Al signal from the alucone coating is uniformly distributed throughout the electrode.
- MLD coating can disperse through the whole electrode despite the tortuous structure.

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# Impact of MLD Coating on Si Anode Electrochemical Performance



Reduction decomposition of the electrolyte is suppressed by the MLD coating, which results in the reduced impedance for the coated electrode.

- ☐ Sustainable cycling only achieved in the coated Si electrodes.
- ☐ Nanoscale Si particles dominate the electrochemical behavior, despite of only 15 wt.% Si used in the electrode.

# RESPONSES TO PREVIOUS YEAR REVIEWER COMMENTS

Last year two poster presentations covered all the project. The two posters were each reviewed by eight reviewers. We thank the reviewers for their thoughtful comments. Selected excerpts are given below.

- Many of the reviewers' comments were generally positive.
  - “applauded the excellent, thorough approach”
  - “very ambitious program to assess advantages, disadvantages and solutions for Si anode materials”
  - “very nice intra-laboratory coordination”
- One reviewer thought we could further enhance the program by bringing in experts in mechanical stresses. We conduct limited mechanical measurements and have relied on literature to establish a stable particle size, but in general we agree more in-depth studies could improve the program.
- One reviewer suggested that our commitment to openness limits our ability to examine proprietary materials. We agree totally and recognize the limitation. However, we consider that the work we are doing is addressing the fundamental issues with silicon materials and will benefit the entire community.

# REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - SEI stability issues, which affect cycling efficiency.
  - Electrode stability issues that include particle isolation, accommodating volume changes, and adherence.

## COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six National Laboratories have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrodes, and cells.
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEI-Sta) project (BAT344, BAT345, BAT346, BAT347, and BAT348).
- Paraclete Energy is supplying baseline silicon materials.

# FUTURE WORK

## Future Efforts Focused on Building and Expanding Early Materials Development Studies

- Further optimization of the Si/CNT hierarchical structure and thermite reactions to control the porosity and hence the electrochemical performance.
  - Explore composite electrodes with controlled graphite ratio.
  - Further optimize the chemical reduction method for Sn-Si phase; focus on the development of Si-Me thin films/splats.
  - Investigate the low capacity obtained for the silicate-coated Si NPs and study the long-term cycling stability of silicate-coated Si electrodes.
  - Form other silicate layers (such as  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{Si}_2\text{O}_5$ ) on the surface of Si nanoparticles and study their effects on the electrochemical property.
  - Further study the impact of functional group on the surface of Si NPs and explore new electrolyte/additive for Si anode/electrolyte stabilization.
- 
- Continue the divergent/convergent approach to further advance the materials developments.
  - Continue in-depth understanding of the Si electrode degradation mechanisms from the material perspective using sophisticated *in-situ* and *ex-situ* diagnosis in collaboration with diagnosis team and post-test facility.
  - Establish general rules dictating the structure-property relationships for Si-based materials and electrodes.
  - Verify the material candidates that showed promising results in a full cell format.
  - Scale up new materials (p-Si/C, Si/CNT/C, Si-Sn alloy, electrolyte/additive) and MLD coated particle and electrode for performance verification.

# SUMMARY

Collaborative multi-National Lab research was performed on the materials and technology development to understand the fundamental phenomena that control the performance of the Silicon composite electrodes.

- ✓ Porous-Si@C was prepared by aluminothermic reduction at  $\sim 200^{\circ}\text{C}$  which showed superior cycling stability and rate capability and retained the spherical morphology after 200 cycles.
- ✓ Hierarchical Si/CNT microspheres were synthesized by aluminothermic reduction of the self-assembled  $\text{SiO}_2$ -CNT microspheres as high performance and low swelling ( $< 30\%$ ) anode materials.
- ✓ Demonstrated  $> 90\%$  capacity retention over 100 cycles for thick electrodes ( $> 2 \text{ mAhcm}^{-2}$ ) in the NMC333 full cell.
- ✓ Chemical reduction method is effective in producing Sn nanoparticles, leading to uniform elemental distribution in the final product. As-produced Si-Sn material exhibited a reversible capacity of  $700 \text{ mAh/g}$  over 200 cycles.
- ✓ Successfully synthesized silicate-coated Si nanoparticles with silicate layers of different thicknesses by *in-situ* XRD.
- ✓ Si particle surface functionalization via silane chemistry and MLD alucone coating.
- ✓ Tailored SEI formation by bi-additive of FEC and silazane and pyrrolidinium-based and fluorinated carbonate based electrolytes.

# CONTRIBUTORS AND ACKNOWLEDGMENT

## Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

## Contributors

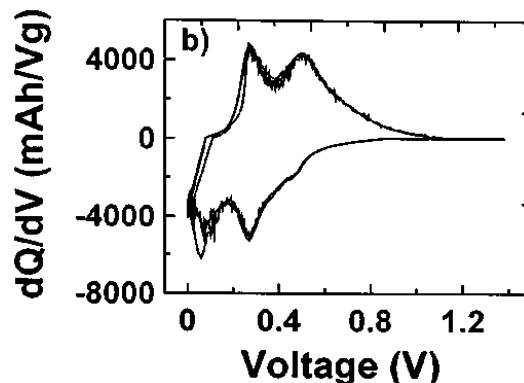
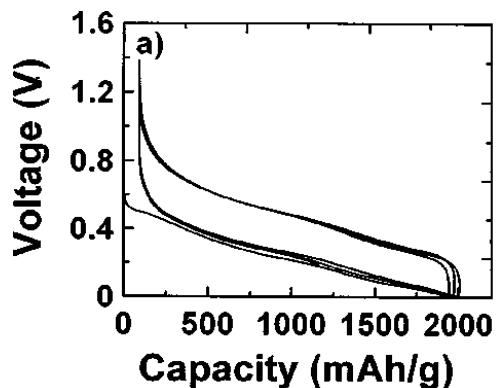
- |                   |                       |                            |                           |
|-------------------|-----------------------|----------------------------|---------------------------|
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| ▪ Eric Allcorn    | ▪ Binghong Han        | ▪ Gao Liu                  | ▪ Caleb Stetson           |
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| ▪ Peng-Fei Cao    | ▪ Gerald Jeka         | ▪ Christopher Orendorff    | ▪ Gabriel Veith           |
| ▪ Yang-Tse Cheng  | ▪ Haiping Jia         | ▪ Bryant Polzin            | ▪ David Wood              |
| ▪ Claus Daniel    | ▪ Sisi Jiang          | ▪ Krzysztof Pupek          | ▪ Yimin Wu                |
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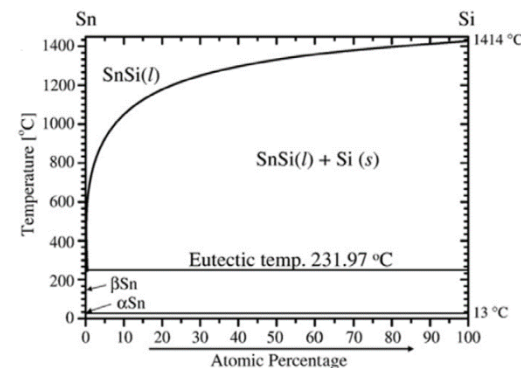
# TECHNICAL BACK-UP SLIDES

## 2. Amorphous $\text{Si}_{0.64}\text{Sn}_{0.36}$

- Amorphous  $\text{Si}_{0.64}\text{Sn}_{0.36}$  thin film exhibits high capacity (2000 mAh/g) with low irreversible capacity (100 mAh/g)
- Immiscible gap between Si and Sn, and low melting point of Sn (232°C) appear to be challenging

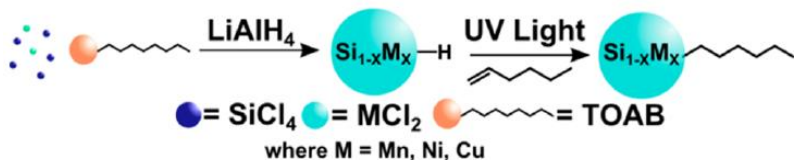


*J. Electrochem. Soc.* **150** (2), A149-A156 (2003)



*J. Phys. D: Appl. Phys.* **47** (2014) 393001

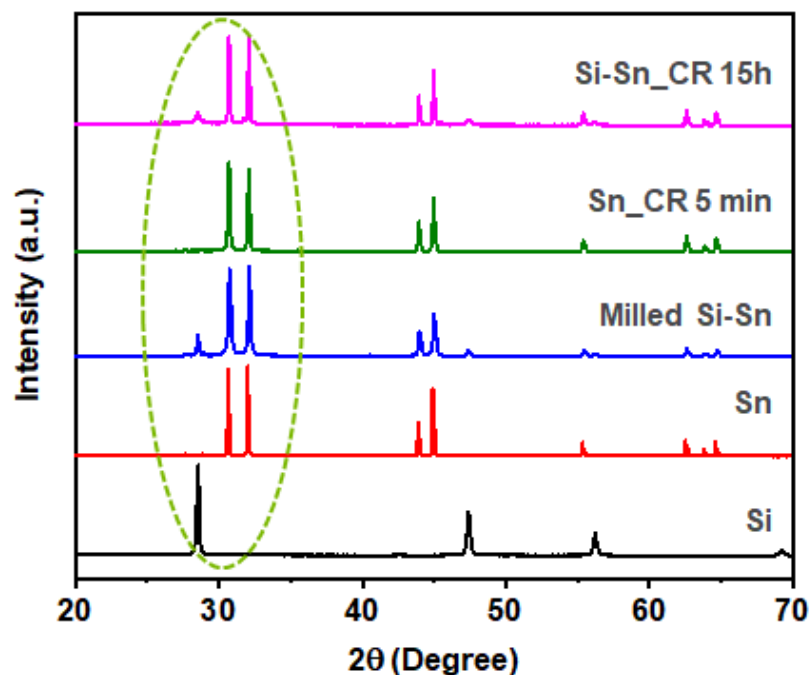
### Chemical Reduction



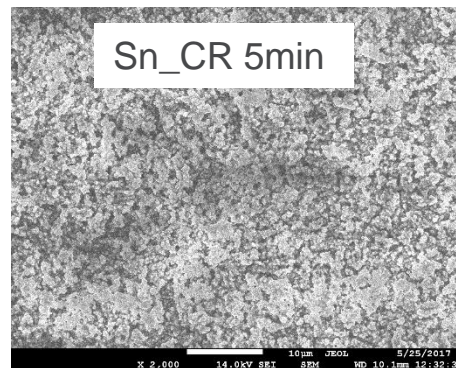
*J. Phys. Chem. Lett.* 2015, **6**, 1573-1576

- ✓ The goal is to achieve optimal performance through the homogeneous mixing of Si and Sn nanoparticles.
- ✓ Reduction of metal salts to produce metal nanocrystals. The liquid-phase reaction facilitates metal mixing.

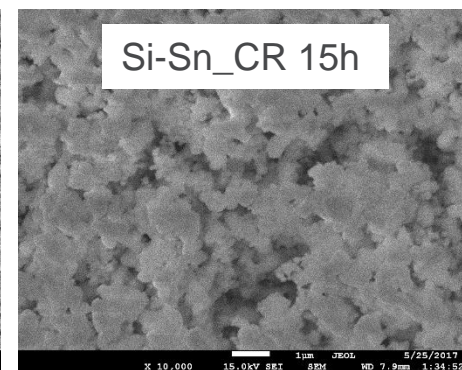
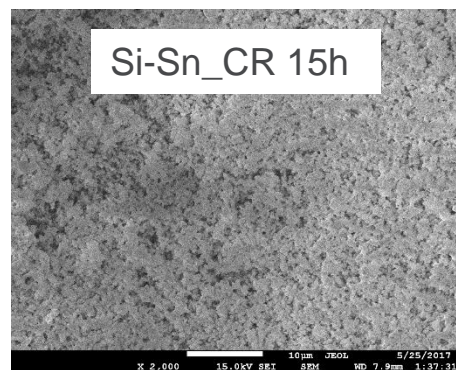
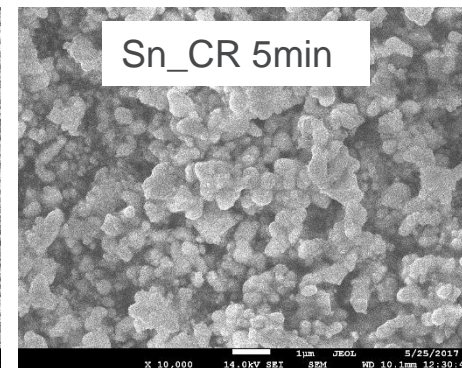
# Synthesis of Si-Sn by Chemical Reduction Reaction



2,000 X (10 μm)



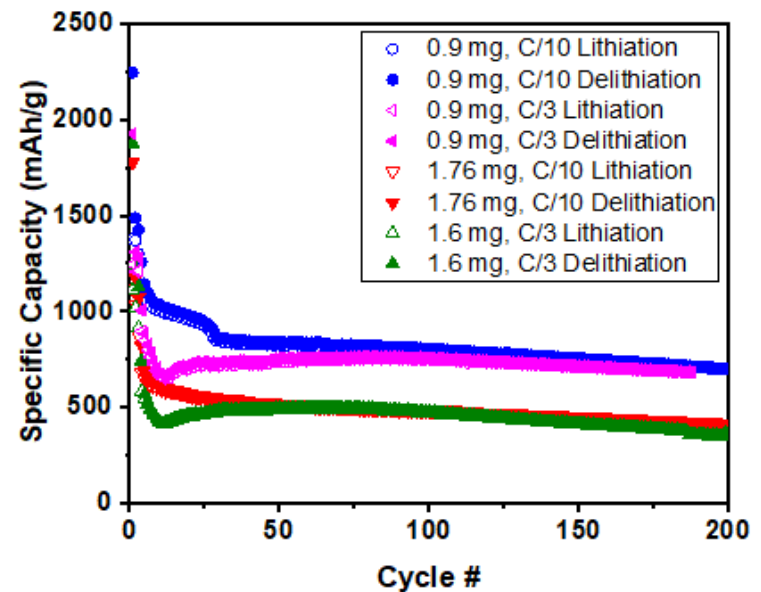
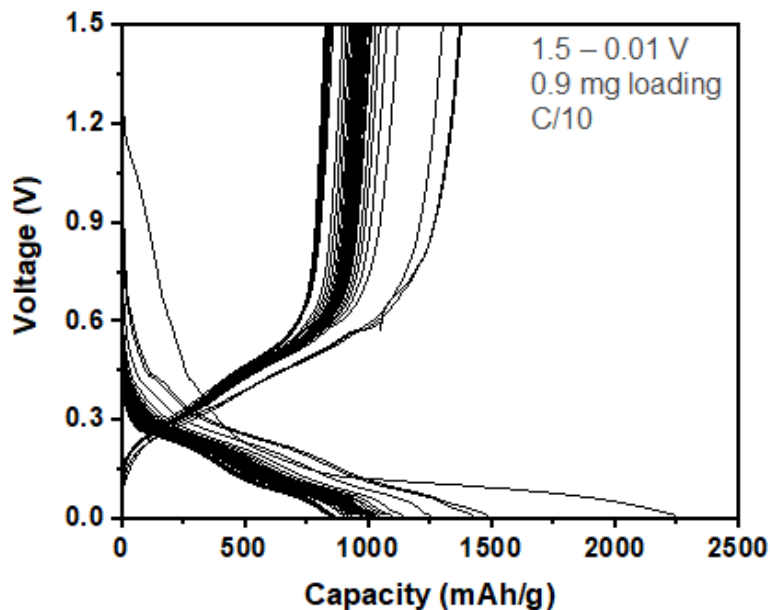
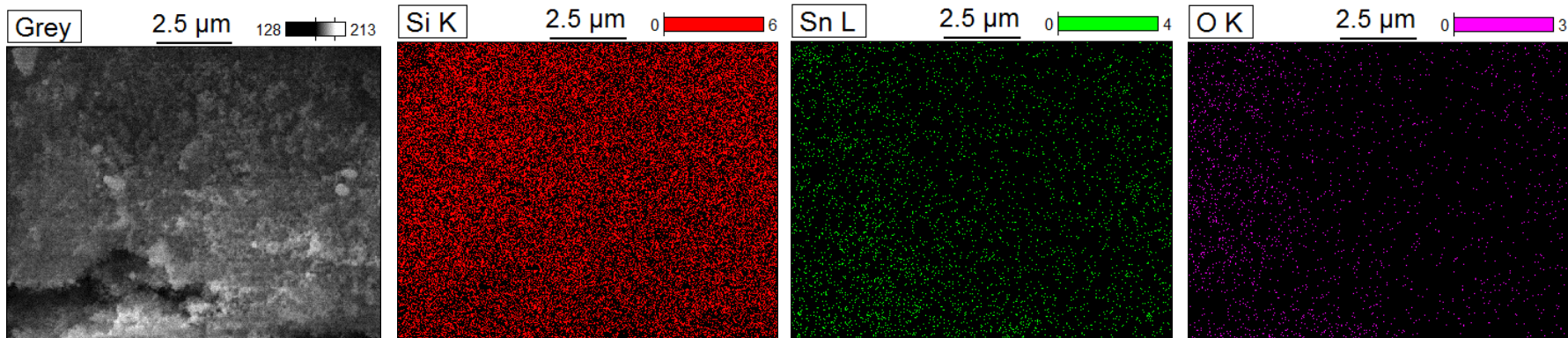
10,000 X (1 μm)



- $\text{SnCl}_2$  solution is added after dispersing Si nanoparticles in  $\text{NaBH}_4$  solution, final product obtained by harvesting insoluble solids, washing and drying under vacuum.
- Pure Sn and Si-Sn phases of a few hundred nanometers successfully prepared by chemical reduction method.

# Elemental Mapping and Electrochemistry of Si-Sn Produced by Chemical Reduction Reaction

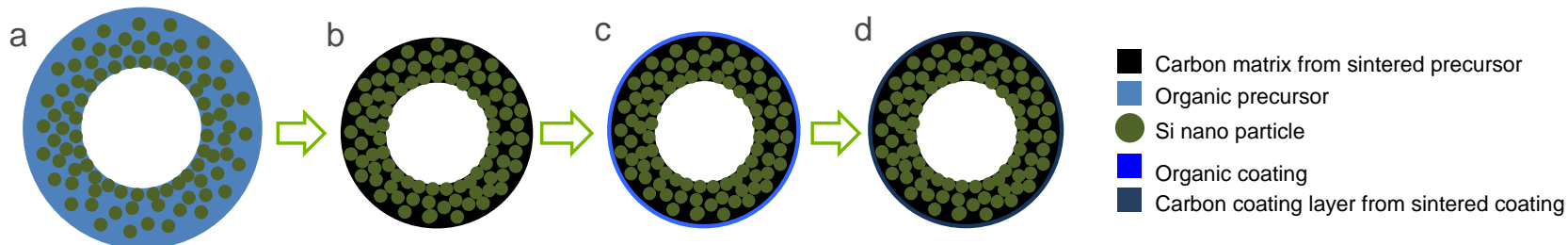
Si-Sn\_CR 15h



- Uniform elemental distribution observed in Sn and Si-Sn phases produced by chemical reduction method; O and Cl residual observed in the final products varied with synthetic conditions.
- Si-Sn sample produced by chemical reduction exhibited an initial capacity of > 1000 mAh/g, with a reversible capacity of ~ 700 mAh/g remained over 200 cycles.

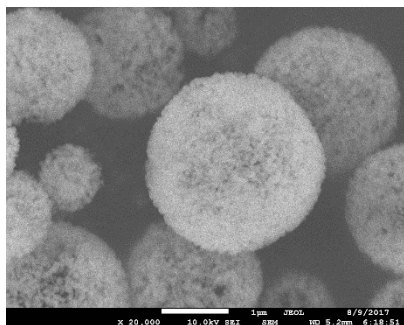
# Template Free Synthesis Of Hollow Core Si Particles

Schematics of the process to make Si/C composite particles

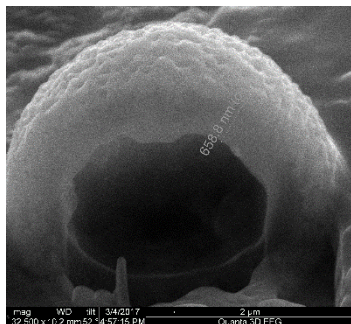


**a.** A hollow core Si nanoparticles. **b.** Si/C composite particles after sintering. **c.** Organic layer coating on the surface of Si/C composite particles. **d.** Carbon coated Si/C composite particle after re-sintering.

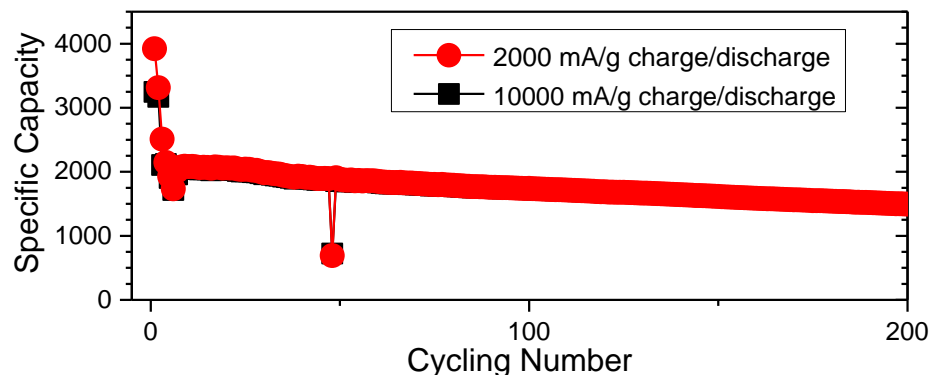
**Micron size particles**



**Hollow core**

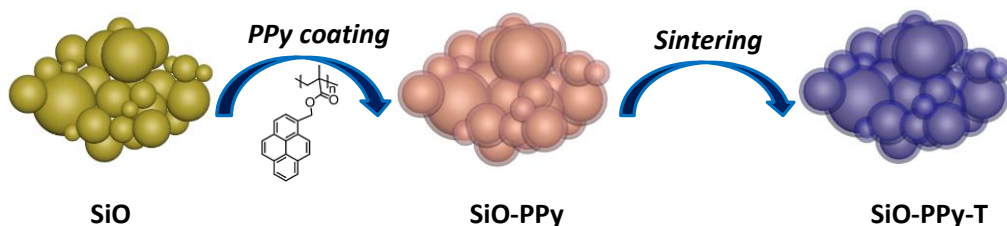


**Cycling performance**

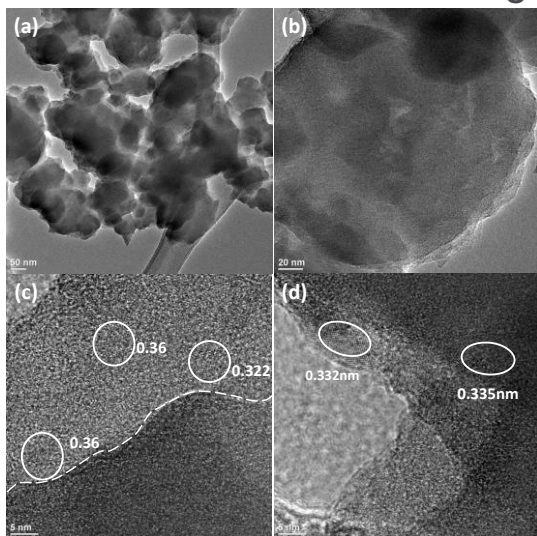


# Si Surface Coating To Improve Cycling Stabilities

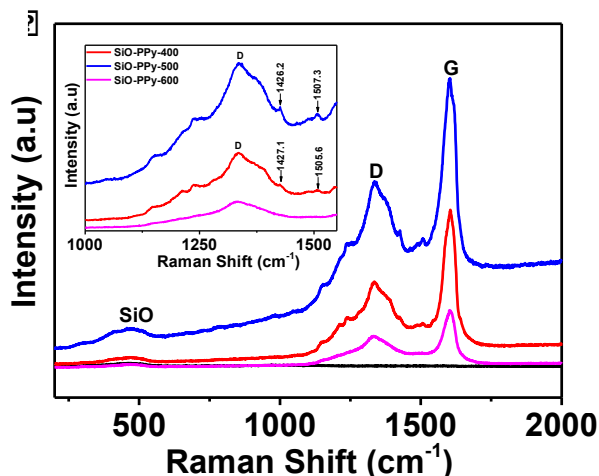
Schematics of surface coating of SiO materials



TEM of the surface coating

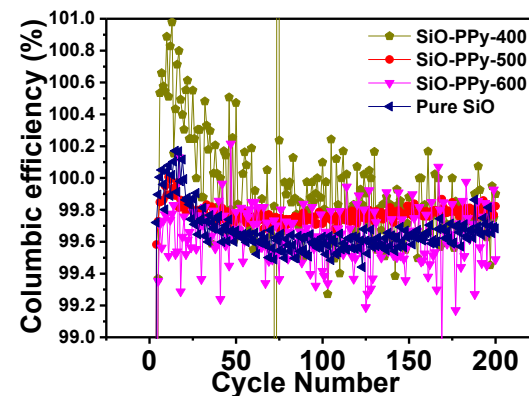
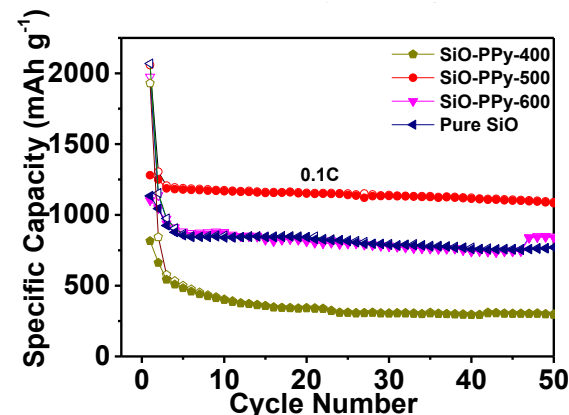


Raman of the surface



The pyrene moieties form pi-pi stacking structure of the polymer. Even at low temperature sintering, the polymer graphitized and formed graphite types of surface coating.

Cycling performance



The low temperature 400°C sintered sample has higher coulombic efficiency.